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IODINE TRANSFER POLYMERIZATION (ITP) OF VINYLIDENE FLUORIDE (VDF). INFLUENCE OF THE DEFECT OF VDF CHAINING ON THE CONTROL OF ITP.

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ABSTRACT

Iodine transfer polymerization (ITP) of vinylidene fluoride (VDF) in the presence of two chain transfer agents (CTA, such as $C_6F_{13}I$ and $HC_2F_4CH_2I$) is presented. Various experimental conditions in terms of the nature of the radical initiators, time, temperature and initial $[initiator]_0/[VDF]_0$ and $[CTA]_0/[VDF]_0$ molar ratios influenced the yield of the reaction, the obtained average degree of polymerization in number, \overline{DP}_n , of PVDF-I, the defect of VDF-chaining and the CX_2I functionality (where $X = H$ or F). The microstructures of these produced PVDF-I oligomers were characterized by 1H and ^{19}F NMR spectroscopy which enabled one to assess the \overline{DP}_n values and to quantify the head-to-head or tail-to-tail defects of VDF-chainings. A low amount of defect of chaining in PVDF-I was noted when $C_6F_{13}I$ in contrast to a higher content from $HC_2F_4CH_2I$. These PVDF-Is exhibited a favored - CH_2CF_2I functionality from the former CTA while it was not observed from the latter one. A good agreement between the targeted and the obtained \overline{DP}_n values was noted for ITP of VDF in the presence of $C_6F_{13}I$ (representative of normal addition) whereas that carried out from $HC_2F_4CH_2I$ (representative of inverse addition) led to experimental \overline{DP}_n values higher than the targeted ones in all cases. A low conversion of $HC_2F_4CH_2I$ was observed in contrast to $C_6F_{13}I$, which shows a better efficiency as the transfer agent.

INTRODUCTION

In contrast to the radical telomerization of fluoroalkenes¹, the controlled radical polymerization of such halogenated monomers has led to few investigations. Neither atom transfer radical polymerization (ATRP)², nor nitroxide mediated polymerization (NMP)³ of fluoroolefins have been reported in the literature. However, the presence of a chain transfer agent enabled the polymerization to be controlled. Except for one survey involving xanthates⁴, several investigations (mentioned in patent literature mainly) report industrial surveys on the iodine transfer polymerization (ITP) of fluoroalkenes and especially on vinylidene fluoride (VDF) with perfluoroalkyl iodides (R_FI) or with α,ω -diiodoperfluoroalkanes (IR_FI). Indeed, the weak R_FCF₂-I bond, the dissociation energy of which is 45 kJ.mol⁻¹, enables an easy cleavage rendering both the resulting R_FCF₂• radical quite reactive and the perfluoroalkyl iodide as an efficient transfer agent hence producing a further VDF adduct with a -CF₂I end-group. Most chemical industries producing VDF have already protected various discoveries such as the synthesis of thermoplastic elastomers (TPE) pioneered by the Daikin Company in 1979⁵ (producing DaeI[®] TPE⁶⁻⁸), then studied by DuPont^{9,10} and developed later by Ausimont (now Solvay Solexis)¹¹⁻¹³. This breakthrough could be possible by the presence of the chain transfer agent and VDF-containing (co)polymer usually made of a soft block that could initiate a further iodine transfer (co)polymerization of one (or two) monomer(s) leading to a soft-b-hard diblock copolymer or hard-b-soft-b-hard triblock copolymers (or thermoplastic elastomers (TPEs)) from R_FI or I-R_F-I, respectively (Table 1).

Insert Table 1

In contrast to these industrial progresses, few rigorous scientific investigations have been reported in the literature. Only Tatemoto^{1,5,14} supplied valuable data on the properties and applications of block copolymers, but the description lacks information on the microstructure of the obtained PVDF blocks, on the nature of the end-groups, on the defects of VDF chaining of these produced blocks, and on the evidence of the controlled or “living” behavior of such a polymerization.

Since VDF is an asymmetrical monomer, the produced macroradical generated in the propagation step may add onto CF₂ or CH₂ sites, considering that an electroattractive

fluorinated radical should react onto CH₂ site taking into account the polar, electronic and steric effects¹⁵⁻¹⁷. As a matter of fact, it is known that VDF telomers, oligomers, or PVDF contain defects in their microstructures linked to the presence of reversed VDF addition since tail-to-tail, -(CF₂CH₂-CH₂CF₂)-, or head-to-head, -(CH₂CF₂-CF₂CH₂)-, chainings have been observed¹⁸⁻²³. Hence, it was worth considering the consequence of these reversed additions on the control of ITP of VDF. The use of C₆F₁₃I as the chain transfer agent should lead to two kinds of chains: one terminated by -CF₂-I as expected, while the other one exhibits a -CF₂CH₂-I end-group. As a result, quantifying the content of both extremities seems possible. Then, to evaluate the difference of reactivity of both -CF₂-I and -CH₂-I end-groups (arising from the steric and inductive effects), it was worth using another transfer agent, HC₂F₄CH₂I, for ITP of VDF.

The objectives of this article concern the study of the iodine transfer polymerization (ITP) of VDF with both these different transfer agents and their influence onto the microstructure of the resulting PVDF-I (and hence the correlation between targeted and experimental average degrees of polymerization), the defects of VDF chaining, and the controlled character of ITP polymerization.

EXPERIMENTAL PART

Materials

Vinylidene fluoride and 1,1,1,3,3-pentafluorobutane were kindly supplied by Solvay S.A., Tavaux, France and Brussels, Belgium. Perfluorohexyl iodide (purity 99%) was kindly supplied by Arkema, France. 1,1,2,2-Tetrafluoro-3-iodopropane (99%) was purchased from Aldrich Chimie, (38299 Saint Quentin-Fallavier, France). *Tert*-butylperoxypivalate (TBPPI, purity 75%) and the 2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane (DHBP, 90%) were gifts from “La Chalonnaise des Peroxydes”, Chalons sur Marne, France. They were used as supplied just like acetonitrile (99%), dimethylformamide (DMF, 99%), tetrahydrofurane (THF, 99%) and methanol of analytical grade (99.8%), from Aldrich Chimie, 38299 Saint Quentin-Fallavier, France.

Analyses

The compositions and the structures of the oligomers obtained by ITP of VDF were determined by ^{19}F (200 MHz) and ^1H NMR (250 or 400 MHz) spectroscopies. The NMR spectra were recorded on Bruker AC 200, AC 250 and AC 400 instruments, using deuterated acetone, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) as the solvents and tetramethylsilane (TMS) (or CFC_3) as the references for ^1H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^1H (or ^{19}F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of $5\ \mu\text{s}$ for ^{19}F NMR.

Reactions in autoclave

Example of iodine transfer polymerization (ITP) of VDF performed in the presence of 1,1,2,2-tetrafluoro-3-iodopropane at 75°C .

A 160-mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer and a rupture disc, was degassed and pressurized with 30 bar of nitrogen to check eventual leaks; then, a 20 mm Hg vacuum was operated for 30 min. Under vacuum, were transferred into the autoclave 0.43 g (2×10^{-3} mol) of *tert*-butylperoxypivalate, 5.04 g (2×10^{-2} mol) of 1,1,2,2-tetrafluoro-3-iodopropane and 100.0 g of 1,1,1,3,3-pentafluorobutane. Then, by mean of double weighing, 19.50 g (30×10^{-2} mol) of VDF were introduced in the mixture. Then, the autoclave was progressively heated to 75°C . There was an exotherm of ca.

10 °C, followed by an increase of pressure from 20 bar up to 26 bar and then a sharp drop of pressure until to 20 bar was noted. After reaction, the autoclave was placed in an ice bath for about 60 minutes and 3.90 g of unreacted VDF were progressively released (the conversion of VDF was 80 %, and the chain transfer constant (CTA) conversion was 33 %). After opening the autoclave, about 120.0 g of a brown liquid were obtained. After evaporation of 1,1,1,3,3-pentafluorobutane, the sample was dissolved in dimethylformamide (DMF), which enabled solubilization of both low average number degree of polymerization (\overline{DP}_n) (also soluble in acetone) and high \overline{DP}_n , and polymers produced were precipitated by adding water into the DMF solution. White powders were obtained in all cases and ^{19}F NMR led to a \overline{DP}_n value of 35. The sample was characterized by ^{19}F and ^1H NMR spectroscopy.

The same procedure was used for the ITP reaction of VDF with perfluorohexyl iodide (supporting information).

NMR characteristics are reported in Tables 2 and 3.

Insert Table 2

Insert Table 3

RESULTS AND DISCUSSION

1-Introduction on ITP

Iodine transfer polymerization (ITP) of vinylidene fluoride deals with the “degenerative transfer” as reversible addition fragmentation transfer (RAFT)²⁴ or macromolecular design for interchange of xanthate^{25,26}. This is an extension of the telomerization^{1,27} taking into account the major difference that the macromolecular chains having undergone a transfer reaction may be involved in a further reaction.

As for the telomerization, ITP requires a chain transfer agent (CTA), and in that present case, an 1-iodofluoroalkane was chosen. Scheme 1 depicts the different steps of ITP of a M monomer.

Insert Scheme 1

The initiating radical, A^\bullet , is generated by thermal decomposition of a conventional initiator, such as *tert*-butylperoxypivalate or 2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane, in step (a). Then, A^\bullet radical reacts onto monomer (M) in step (b), followed by propagation of M as shown in step (c). The exchange of iodine from the transfer agent, R_F-I , to the propagating radical, P_n^\bullet , results in the formation of the polymeric alkyl iodide, P_n-I , and a new initiating radical, R^\bullet (step (d)). Large differences in the stability of the reactants and products involved in step (e) could result in shifting the equilibrium overwhelmingly to the right or to the left. Therefore, the ideal case is when the structure of R_F closely resembles the structure of the propagating radical, resulting in a thermodynamically neutral transfer step. The exchange process described in step (e) is thermodynamically neutral, because P_n and P_m propagating chains are identical. Step (e) shows an equilibrium between dormant and living species which is crucial^{1,3} for a *pseudoliving* behavior. As in any radical process, reaction of termination occurs, such as disproportionation and coupling of macroradicals (step f). But, to preserve the living or controlled behavior, the termination reaction (f) must be negligible about the transfer ones (this condition is used for the other controlled radical polymerizations, such as ATRP, RAFT, or MADIX) and two key parameters must be taken into account:

i) the initiator amount must be as low as possible to avoid any presence of dormant (or dead) chains but in efficient amount to initiate that radical reaction. However, that amount depends upon the purity of the chain transfer agent. Actually, traces of iodine in the medium may allow an overconsumption of initiator and an inhibition time may occur²⁸.

ii) The CTA amount enables to control the molar masses of the produced polymers. In the ideal case of a total conversion of CTA, the theoretical number average degree of polymerization (\overline{DP}_n) can be assessed from Equation (1) :

$$\overline{DP}_n = \frac{\alpha_{VDF} [VDF]_0}{[CTA]_0} \quad (1)$$

where $[VDF]_0$, $[CTA]_0$ and α_{VDF} represent the monomer and CTA concentrations in feed and the VDF conversion, respectively.

The reactivity of CTA can be controlled by carrying out different reactions that make varying the theoretical (or targeted) \overline{DP}_n s and to compare them with those obtained experimentally. A satisfactory agreement between these values enables one to confirm the good reactivity of the CTA.

2-Results

Iodine transfer polymerization of vinylidene fluoride was initiated by *tert*-butylperoxypivalate (TBPPI), in the presence of a iodofluorinated chain transfer agent ($C_6F_{13}I$ and $HC_2F_4CH_2I$) and in 1,1,1,3,3-pentafluorobutane at 75 °C for 4 hrs. After reaction and elimination of both the solvent and the CTA under vacuum, PVDF-I was precipitated from water. Its experimental \overline{DP}_n value was assessed from ^{19}F and 1H NMR spectroscopy.

2-1. ITP of VDF with $C_6F_{13}I$

As expected, the ^{19}F NMR spectrum (Figure 1) exhibits, beside the absence of the multiplet centered at -60.0 ppm attributed to $-CF_2\overline{C}E_2I$ of $C_6F_{13}I$ that has undergone a high field shift to -112.0 ppm, the characteristic signals of C_5F_{11} end-group centered at -82.0, -124.0, -126.0 and -128.0 ppm assigned to CF_3 and the four CF_2 groups, respectively²⁹⁻³¹. The major signal centered at -91.0 ppm is attributed to difluoromethylene groups $-CH_2\overline{C}E_2-CH_2\overline{C}E_2-CH_2CF_2-$ (i.e. normal head-to-tail VDF-chaining).

Insert Figure 1

The presence of the triplet (${}^3J_{FH} = 7.0$ Hz) of triplets (${}^4J_{FF} = 9.8$ Hz) centered at -38.0 ppm evidences the expected $-\text{CH}_2\text{CF}_2\text{I}$ end-group (e) while both signals at -108.0 ppm (e') correspond to the difluoromethylene in $-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2\text{I}$ group^{19-23,29}, arising from a reversed addition followed by a transfer step.

Indeed, Scheme 2 illustrates the different reactions that occur in ITP of VDF and enable to understand the defects of VDF chaining. Surprisingly, the ${}^{19}\text{F}$ NMR spectrum (Figure 1) shows only traces of both multiplets centered at -113.0 and -116.0 ppm assigned to $-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$ reversed head-to-head addition, respectively, as usually observed in VDF-containing telomers^{20-22,29}, oligomers^{19,21,23} or polymers^{23,32}.

Insert Scheme 2

${}^1\text{H}$ NMR spectrum of that same sample (Figure 2) confirms the statements above. Methylene groups located between two difluoromethylenes led to a quintet centered at about 3.0 ppm while the signals centered at 3.3, 3.6 and 3.9 ppm are attributed to methylene groups in $\text{C}_6\text{F}_{13}\text{CH}_2-$, $-(\text{VDF})_n\text{CH}_2\text{CF}_2\text{I}$, and $-\text{CF}_2\text{CH}_2\text{I}$ ^{29,31,33}, respectively.

Insert Figure 2

As expected, $-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$ reverse tail-to-tail additions are noted by the presence of a broad signal centered at 2.5 ppm^{19-23,32,33}, although their integrals are small for low $\overline{\text{DP}}_n$ and increase for higher $\overline{\text{DP}}_n$. Interestingly, the absence of triplets centered at 1.2 and 1.8 ppm characteristic of methyl end-groups in $\text{CH}_3\text{CH}_2\text{CF}_2-$ and $\text{CH}_3\text{CF}_2\text{CH}_2-$ groups^{20,23}, respectively, evidences the absence of the direct initiation of $\cdot\text{CH}_3$ (arising from $(\text{CH}_3)_3\text{CO}\cdot$ generated by *tert*-butylperoxypivalate) and $(\text{CH}_3)_3\text{C}\cdot$ onto VDF as previously observed²³.

$\overline{\text{DP}}_n$ values can be assessed from ${}^1\text{H}$ and ${}^{19}\text{F}$ NMR spectra :

i) from ${}^1\text{H}$ NMR, taking into account the integrals of the signal attributed to methylene groups ($\int\text{CH}_2$) in PVDF about those of CH_2 adjacent to C_6F_{13} end-groups, as follows :

$$\overline{\text{DP}}_n = \frac{\int\text{CH}_2^{2.5\text{ppm}} + \int\text{CH}_2^{3.0\text{ppm}} + \int\text{CH}_2^{3.3\text{ppm}} + \int\text{CH}_2^{3.6\text{ppm}} + \int\text{CH}_2^{3.9\text{ppm}}}{\int\text{CH}_2^{3.3\text{ppm}}} \quad (2)$$

ii) from ^{19}F NMR spectrum (Figure 1) taking into account the integrals of signals of CF_2 assigned to PVDF centered at -91.0ppm, -38.0 ppm and -108.0 ppm about that of CF_3 end-group centered at -82.0 ppm, as follows :

$$\overline{DP}_n = \frac{\int \text{CF}_2^{-91.0\text{ppm}} / 2 + \int (\text{CF}_2^{-38.0\text{ppm}} + \text{CF}_2^{-108.0\text{ppm}}) / 2 + \int \text{CF}_2^{-112.0\text{ppm}} / 2}{\int \text{CF}_3^{-82.0\text{ppm}} / 3} \quad (3)$$

Table 4 represents the experimental reactant molar ratios, the targeted and experimental \overline{DP}_n values and the theoretical and experimental functionalities (in iodine).

Indeed, the obtained values of \overline{DP}_n are slightly lower than those expected. This difference can be explained by a non-total conversion of VDF (in the 70-90% range).

Actually, in the course of the propagation step of ITP, the reactivity of $\text{---CH}_2\text{CF}_2\cdot$ macroradical onto VDF can lead either to a normal or reverse addition (Scheme 2). Transfer steps of the produced macroradicals hence yield $\text{---CH}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{I}$ and $\text{---CH}_2\text{CF}_2\text{-CF}_2\text{CH}_2\text{I}$, for which the characteristic signals of both CF_2 end-groups appear at -38.0 and -108.0 ppm, respectively.

Therefore, the functionalities in $-\text{CF}_2\text{I}$ and $-\text{CF}_2\text{CH}_2\text{I}$ can be assessed from NMR by following equations (4) and (5) :

$$\text{functionality}^{-\text{CF}_2\text{-I}} = \frac{\int \text{CF}_2\text{-I}^{-38.0\text{ppm}} / 2}{\int \text{CF}_3^{-82.0\text{ppm}} / 3} \quad (4\text{-a})$$

Equations (4-a) and (4-b) enable one to determine the functionalities in $-\text{CF}_2\text{I}$ and $-\text{CF}_2\text{CH}_2\text{I}$ by ^{19}F NMR, respectively.

$$\text{functionality}^{-\text{CF}_2\text{CH}_2\text{-I}} = \frac{\int \text{CF}_2^{-108.0\text{ppm}} / 2}{\int \text{CF}_3^{-82.0\text{ppm}} / 3} \quad (4\text{-b})$$

The experimental values of such functionalities (Table 4) can be compared to those determined by ^1H NMR taking into account the characteristic signals of $-\text{CF}_2\text{CH}_2\text{I}$, $-\text{CH}_2\text{CF}_2\text{I}$ and $\text{C}_6\text{F}_{13}\text{CH}_2(\text{VDF})_n\text{I}$ noted at 3.9, 3.7 and 3.3. ppm, respectively, as follows :

$$functionality^{-CF_2-I} = \frac{\int -\underline{CH_2}-CF_2-I^{3.7ppm} / 2}{\int RF-\underline{CH_2}-CF_2-(VDF)_n-I^{3.3ppm} / 2} \quad (5-a)$$

$$functionality^{-CF_2CH_2-I} = \frac{\int -CF_2-\underline{CH_2}-I^{3.9ppm}}{\int RF-\underline{CH_2}-CF_2-(VDF)_n-I^{3.3ppm}} \quad (5-b)$$

Equations (5-a) and (5-b) also allow one to assess the functionalities in $-CF_2I$ and $-CF_2CH_2I$ by 1H NMR, respectively.

Table 4 also lists the functionalities of PVDF-I in $-CF_2I$ and $-CF_2CH_2I$ and shows a good agreement of these values calculated from ^{19}F or 1H NMR spectroscopy. This table also shows that $-CF_2I$ functionality regularly decreases for higher targeted \overline{DP}_n . Indeed, this drop of functionality arises from the reversed addition of the macroradical onto VDF in the propagation step. The literature reports various defects of chaining, usually ranging between 6 and 9% for PVDF^{32,34,35} or for oligo(VDF)^{19,21,23} and 5-10% for VDF telomers^{1,20,22,29,31}, although a recent work reports a value of 2.5% from fractionated $CF_3(VDF)_nI$ telomers³³.

Insert Table 4

Equation (6) supplies the theoretical functionality linking the content of chains that do not undergo any inversion (ψ) and the n number of VDF units, taking into account that the addition of $C_6F_{13}^\bullet$ onto VDF is regioselective and always occurs as a normal addition^{29,31,33} hence showing a “n-1” value in equation (6) :

$$\text{Theoretical functionality in } CF_2-I = (\psi)^{(n-1)} \quad (6)$$

By varying ψ value, the rate of reverse addition can be determined for each addition onto a further VDF (Table 4). The obtained value is close to 95% (this value gives the best fitting with the experimental values). Indeed, for a PVDF-I of \overline{DP}_6 , 77% of $-CF_2I$ end-groups has been observed experimentally, while for PVDF-I of \overline{DP}_{13} , $-CF_2I$ theoretical (from Equation (6)) and experimental contents are identical (54%). These values show that the reverse addition of VDF is not disturbed by ITP. Hence, mechanism of ITP does not prevent from limiting the inversions.

Then, the fractionation of produced PVDF-I (\overline{DP}_{25}) was carried out in acetone then in methanol to separate higher from lower molecular weight-PVDF-I (Table 5). Such a procedure enabled us to assess the distribution of oligomers bearing -CF₂I end-group.

Interestingly, low \overline{DP}_n fractions (i.e., F1 and F2) contain PVDF-I bearing -CF₂CH₂I end-group exclusively as evidenced by ¹⁹F and ¹H NMR (Table 5). This observation can be explained by two features :

- i) -CH₂I end group is totally unreactive and can not lead to any transfer reaction thus stopping the polymerization ;
- ii) -CH₂I is far less reactive than -CF₂I ; hence the presence of -CF₂I end group in the medium still enables further transfer reactions. For a better understanding of that reaction, it was worth attempting an ITP of VDF with a chain transfer agent bearing a -CF₂CH₂I end group, described below.

Insert Table 5

2-2 ITP of VDF in the presence of HC₂F₄CH₂I

The structure of HCF₂(CF₂CH₂)I exhibits a VDF unit adjacent to an iodine end-group as frequently involved in controlled radical polymerization¹⁻³.

A reaction was carried out as above starting from the following initial concentration molar ratios : [VDF]₀ : [CTA]₀ : [TBPPI]₀ = 100.0 : 6.6 : 0.6. After reaction, a sample was taken off from the total product mixture and was characterized by NMR. The remaining solution was evaporated, precipitated from water and dried under vacuum at 60 °C for 24 hrs. The obtained polymer was also characterized by NMR. In contrast to the absence of C₆F₁₃I observed in the case above, the presence of unreacted HC₂F₄CH₂I was noted by means of ¹H (presence of a triplet of triplets and of a quintet centered at 6.5 and 3.6 ppm, respectively) and ¹⁹F NMR (presence of a triplet (³J_{FF} = 17.8 Hz) of quartets (³J_{HF} = 3.4 Hz) and of a doublet (²J_{HF} = 49.6 Hz) of triplets (³J_{HF} = 4.0 Hz) centered at -112.0 and -136.0 ppm, assigned to -CF₂CH₂I and HCF₂-, respectively).

Figure 3 exhibits the ¹⁹F NMR spectrum of the sample produced from ITP of VDF with HC₂F₄CH₂I for which the characteristic signal (assigned to HCF₂- end-group) of the unreacted CTA is located at -136.0 ppm. After ITP of VDF, the signal of HCF₂- group underwent a slight high field shift from -136.0 ppm (unreacted CTA) to -138.0 ppm. In

addition, this spectrum shows that the chemical shifts assigned to CF₂ groups of incorporated VDF were similar to those of PVDF-I (Figure 3), just like the other methylene in the CTA.

Insert Figure 3

Thus, \overline{DP}_n value was assessed from the integrals of the characteristic signals about that of HCF₂- end-group, as follows (eq. 7) :

$$\overline{DP}_n = \frac{\int CF_2^{-91.0ppm} + \int CF_2^{-95.0ppm} + \int (CF_2^{-38.0ppm} + CF_2^{-108.0ppm}) + \int CF_2^{-112ppm} + \int CF_2^{-115ppm}}{\int CF_2^{-138.0ppm}} \quad (7)$$

Figure 3 shows the absence of the signal located at -38.0 ppm assigned to -CF₂CH₂I.

¹H NMR spectrum (Figure 4) also exhibits the characteristic signal centered at 6.5 ppm attribute to HCF₂CF₂-, while the other signals assigned to the methylene groups are similar to those noted in the ¹H NMR spectra of the above C₆F₁₃-PVDF-I. The signal centered at 6.5 ppm shows a complex shape, because there is an overlapping of two triplets of triplets which have different coupling constants: HCF₂CF₂- assigned from chain transfer agent, which appears at 6.5 ppm and HCF₂CH₂- from transfer reaction, which appears at 6.3 ppm, as expected. However, the defects of chaining (tail-to-tail adducts evidenced by the broad multiplet centered at 2.6 ppm) are in a higher amount in these HC₂F₄CH₂-PVDF-I polymers (Figure 4). The presence of signals centered at 1.0, 1.2, 1.3 and 1.8 ppm shows the direct initiation of CH₃• and C(CH₃)• (generated than the decomposition of *tert*-butylperoxy pivalate)²³ onto VDF. This initiator decomposition generates two radicals: (CH₃)₃C• and *tert*-butoxyradicals ((CH₃)₃CO• that rearrange to produce CH₃• radical and acetone (Scheme 3).

Insert Scheme 3

As shown earlier²³, CH₃• and (CH₃)₃C• radicals can be added onto CH₂ or CF₂ sites of VDF. Thus, these different additions leading to four structures : (CH₃)₃C-CH₂-CF₂-, CH₃-CH₂-CF₂-, (CH₃)₃C-CF₂-CH₂- and CH₃-CF₂-CH₂- end-groups evidenced by signals (¹H NMR) at 1.0, 1.2, 1.3 and 1.8 ppm, respectively (Figure 4). The structure CH₃-CH₂-CF₂- is confirmed by the signal centered at -95.7 ppm in ¹⁹F NMR spectrum, while the other signals ((CH₃)₃C-CH₂-CF₂-

, $\text{CH}_3\text{-CF}_2\text{-CH}_2\text{-}$ and $(\text{CH}_3)_3\text{C-CF}_2\text{-CH}_2\text{-}$) are overlapping with other signals in ^{19}F NMR spectrum.

Insert Figure 4

As in equation 7, $\overline{\text{DP}}_n$ values were assessed from the integrals of all methylene groups, taking into account that of “labeled” $\text{HCF}_2\text{-}$, $\text{CH}_3\text{-CF}_2\text{-CH}_2\text{-}$, $(\text{CH}_3)_3\text{C-CH}_2\text{-CF}_2\text{-}$, $\text{CH}_3\text{-CH}_2\text{-CF}_2\text{-}$ and $(\text{CH}_3)_3\text{C-CF}_2\text{-CH}_2\text{-}$ end-groups (Eq. 8) :

$$\overline{\text{DP}}_n = \frac{(\int \text{CH}_2^{2.3\text{ppm}} + \int \text{CH}_2^{2.9\text{ppm}} + \int \text{CH}_2^{3.9\text{ppm}}) / 2}{\int \text{HCF}_2^{6.5\text{ppm}} + \frac{\int \text{CH}_3\text{-CH}_2^{1.2\text{ppm}} + \int \text{CH}_3\text{-CF}_2^{1.8\text{ppm}}}{3} + \frac{\int (\text{CH}_3)_3\text{C-CH}_2^{1.0\text{ppm}} + \int (\text{CH}_3)_3\text{C-CF}_2^{1.3\text{ppm}}}{9}} \quad (8)$$

The experiments were carried out at 75 and 135 °C, initiated by *tert*-butylperoxypivalate (TBPPI) and 2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane (DHBP), respectively. The targeted and experimental values of $\overline{\text{DP}}_n$ for ITP reaction performed with various concentrations of $\text{HCF}_2(\text{CF}_2\text{CH}_2)\text{I}$ are listed in Table 6. A major difference is noted between targeted and obtained $\overline{\text{DP}}_n$ values. This discrepancy arises from the low CTA conversion (i.e., 33% was reacted) with respect to the low reactivity of this CTA.

Insert Table 6

A major difference is noted between the $\overline{\text{DP}}_n$ values obtained from ^1H and ^{19}F NMR. This difference can be explained by direct initiation of (TBPPI or DHBP) initiator. ^{19}F NMR does not allow taking into account the chains resulting from direct initiation. The interval of confidence of $\overline{\text{DP}}_n$ values obtained from ^{19}F NMR is about 10-15 %.

^1H NMR, enables one to quantify the chain percentage (ϵ) resulting from direct initiation. Thus, the rate of direct initiation was evaluated from ^1H NMR, by equation 9. The percentage of the CTA end-chain is shown by the $\text{HCF}_2\text{CF}_2\text{-}$ signal which appears at 6.5 ppm. This is possible since it is assumed that in these conditions, $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ does not lead to any transfer, hence avoiding the formation of characteristic $\text{-CH}_2\text{CF}_2\text{-H}$ end-group which appears as a triplet to triplets centered at 6.3 ppm^{20,21,23}. This is confirmed by the absence of

the characteristic doublet of multiplets centered at -114.8 ppm^{20,21,23} in the ^{19}F NMR spectrum.

$$\varepsilon = \frac{\int (\underline{\text{CH}_3})_3\text{C}-\text{CH}_2^{1.0\text{ppm}} + \int (\underline{\text{CH}_3})_3\text{C}-\text{CF}_2^{1.3\text{ppm}}}{9} + \frac{\int \underline{\text{CH}_3}-\text{CH}_2^{1.2\text{ppm}} + \int \underline{\text{CH}_3}-\text{CF}_2^{1.8\text{ppm}}}{3} \quad (9)$$

$$\varepsilon = \frac{\int (\underline{\text{CH}_3})_3\text{C}-\text{CH}_2^{1.0\text{ppm}} + \int (\underline{\text{CH}_3})_3\text{C}-\text{CF}_2^{1.3\text{ppm}}}{9} + \frac{\int \underline{\text{CH}_3}-\text{CH}_2^{1.2\text{ppm}} + \int \underline{\text{CH}_3}-\text{CF}_2^{1.8\text{ppm}}}{3} + \int \underline{\text{HCF}_2}^{6.5\text{ppm}}$$

ε Values are summarized in Table 6 and show the low efficiency of $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ in contrast to that of $\text{C}_6\text{F}_{13}\text{I}$. Hence, it can not lead to a good control of molar masses at 75 °C. This statement can be explained by the dissociation energy of $-\text{CH}_2\text{-I}$ bond which is stronger than that of $-\text{CF}_2\text{-I}$ (ca. $45 \text{ kJ}\cdot\text{mol}^{-1}$). To make lower the stability of $-\text{CH}_2\text{-I}$ bond and hence to improve the transfer step, ITP of VDF with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ was carried out at 135 °C (Table 6). The CTA conversion increased (66%) while the control of the $\overline{\text{DP}}_n$ was slightly improved. However, $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ does not lead to any good control of the molar masses. Deeper experiments are under progress, especially the kinetics of ITP of VDF, to check whether this radical polymerization is controlled or *pseudoliving*.

CONCLUSION

Two fluoroiodinated chain transfer agents involved in the iodine transfer polymerization (ITP) of vinylidene fluoride have shown different behaviors in transfer, leading to different consequences in ITP³⁷. $\text{C}_6\text{F}_{13}\text{I}$ exhibits high efficiency and reactivity, thus inducing a good control of average degree of polymer in number ($\overline{\text{DP}}_n$) and a few defects of VDF chaining. Such a reaction is close to a *pseudoliving* polymerization, but to check that observation a deeper study is necessary. In contrast, $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ behaves differently in similar conditions and leads to PVDF-I polymers containing higher defects of VDF chaining and having uncontrolled $\overline{\text{DP}}_n$ (experimental values were almost twice higher than those of the targeted ones). At higher temperatures, greater CTA conversions were noted while a slightly better control of $\overline{\text{DP}}_n$ was achieved. The microstructure of resulting PVDF-I leads to the following conclusions:

- i) ITP of VDF involving $\text{C}_6\text{F}_{13}\text{I}$ produced two structures: $\text{C}_6\text{F}_{13}\text{-(VDF)}_n\text{-CH}_2\text{-CF}_2\text{-I}$ and $\text{C}_6\text{F}_{13}\text{-(VDF)}_n\text{-CF}_2\text{-CH}_2\text{-I}$;

- ii) When the macroradical terminated by $-\text{CH}_2\text{CF}_2^\bullet$ reacts onto CF_2 site of VDF, the generated $-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2^\bullet$ (head to head addition) radical undergoes a transfer which is not able to reinitiate ($-\text{CF}_2-\text{CH}_2-\text{I}$), hence leading to dormant species which stopped the reaction.

However, further investigations are required to understand ITP of VDF (i.e., to check the *pseudoliving* character of ITP by establishing the molar masses *versus* VDF conversion linear relationship) and to study the kinetics of that polymerization. Hence, it is worth assessing the transfer constants of $\text{C}_6\text{F}_{13}\text{I}$, $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ and also $\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{I}$ and to study the “molar masses –VDF conversion” relationships in each case, under investigation.

ACKNOWLEDGMENTS

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SUPPORTING INFORMATION

Supporting Information Available: ^{19}F NMR spectra of $\text{C}_6\text{F}_{13}\text{I}$, $\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{I}$, $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ and of sample produced by ITP of VDF with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Scheme Captions

Scheme 1. Elementary steps of Iodine Transfer Polymerization of M monomer

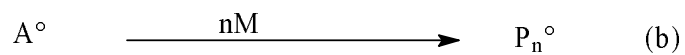
Scheme 2. Different reactions that occur in Iodine Transfer Polymerization of vinylidene fluoride.

Scheme 3. Decomposition of *Tert*-butylperoxypivalate, formation of the radicals and their addition onto vinylidene fluoride²³.

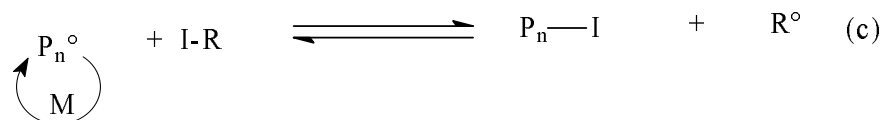
decomposition of (A₂) initiator



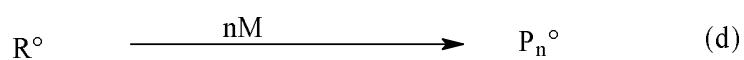
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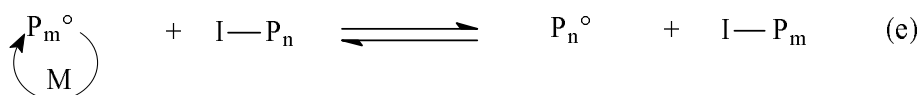
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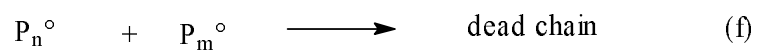
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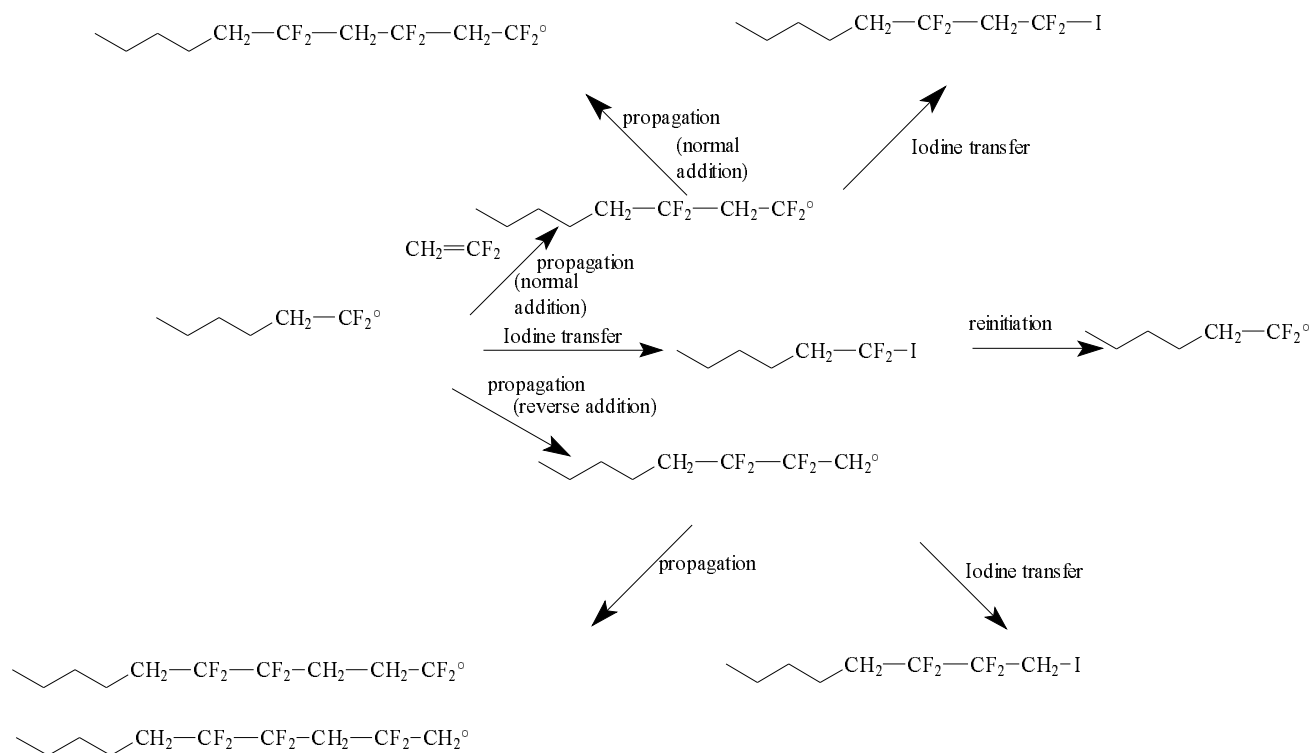
equilibrium between dormant and living species :



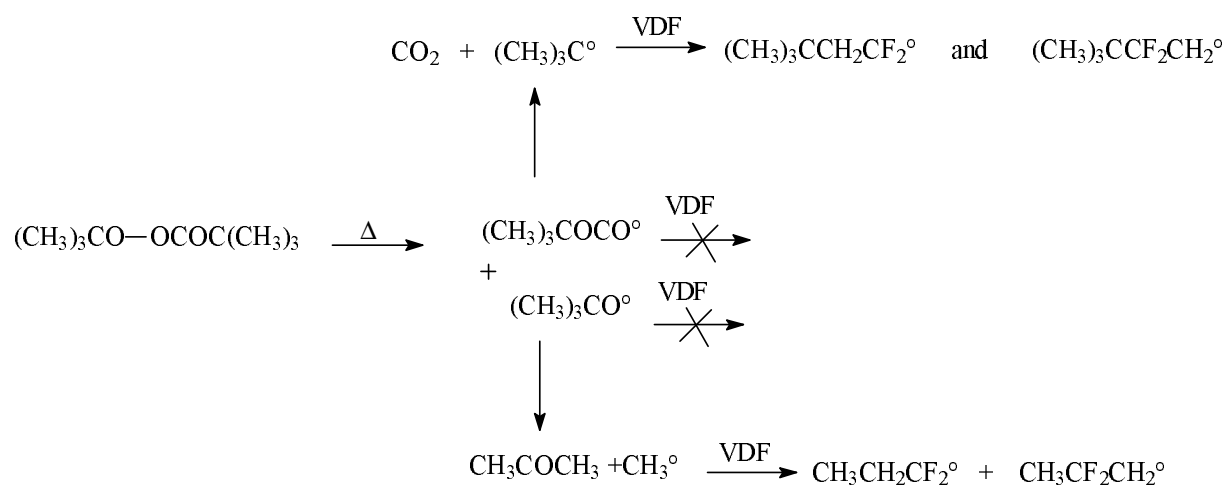
termination :



Scheme 1. Elementary steps of Iodine Transfer Polymerization of M monomer



Scheme 2. Different reactions that occur in Iodine Transfer Polymerization of vinylidene fluoride.



Scheme 3. Decomposition of *Tert*-butylperoxypivalate, formation of the radicals and their addition onto vinylidene fluoride²³.

Figure Captions

Figure 1. ^{19}F NMR spectrum of the poly(vinylidene fluoride)-I (recorded in deuterated acetone; 200 MHz, 298 K) (Average number degree of polymerization ($\overline{\text{DP}}_n$) = 13).

Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{C}_6\text{F}_{13}\text{I}$: $[\text{VDF}]_0 : [\text{C}_6\text{F}_{13}\text{I}]_0 : [\text{Tert-butylperoxypivalate}]_0 = 100.0 : 6.6 : 0.6$ at 75°C .

Figure 2. ^1H NMR spectrum of the poly(vinylidene fluoride)-I after precipitation (recorded in deuterated acetone; 200 MHz, 298 K) (Average number degree of polymerization ($\overline{\text{DP}}_n$) = 13).

Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{C}_6\text{F}_{13}\text{I}$: $[\text{VDF}]_0 : [\text{C}_6\text{F}_{13}\text{I}]_0 : [\text{Tert-butylperoxypivalate}]_0 = 100.0 : 6.6 : 0.6$ at 75°C .

Figure 3. ^{19}F NMR spectrum of poly(vinylidene fluoride)-I obtained by *Iodine Transfer Polymerization* of vinylidene fluoride with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ (after precipitation and purification) (Average number degree of polymerization ($\overline{\text{DP}}_n$) = 35, calculated from Equation 8) (recorded in deuterated dimethylformamide; 250 MHz, 298 K).

Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$: $[\text{VDF}] : [\text{HC}_2\text{F}_4\text{CH}_2\text{I}] : [\text{Tert-butylperoxypivalate}] = 100.0 : 6.6 : 0.6$ at 75°C .

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Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$: $[\text{VDF}]_0 : [\text{HC}_2\text{F}_4\text{CH}_2\text{I}]_0 : [\text{Tert-butylperoxypivalate}]_0 = 100.0 : 6.6 : 0.6$ at 75°C .

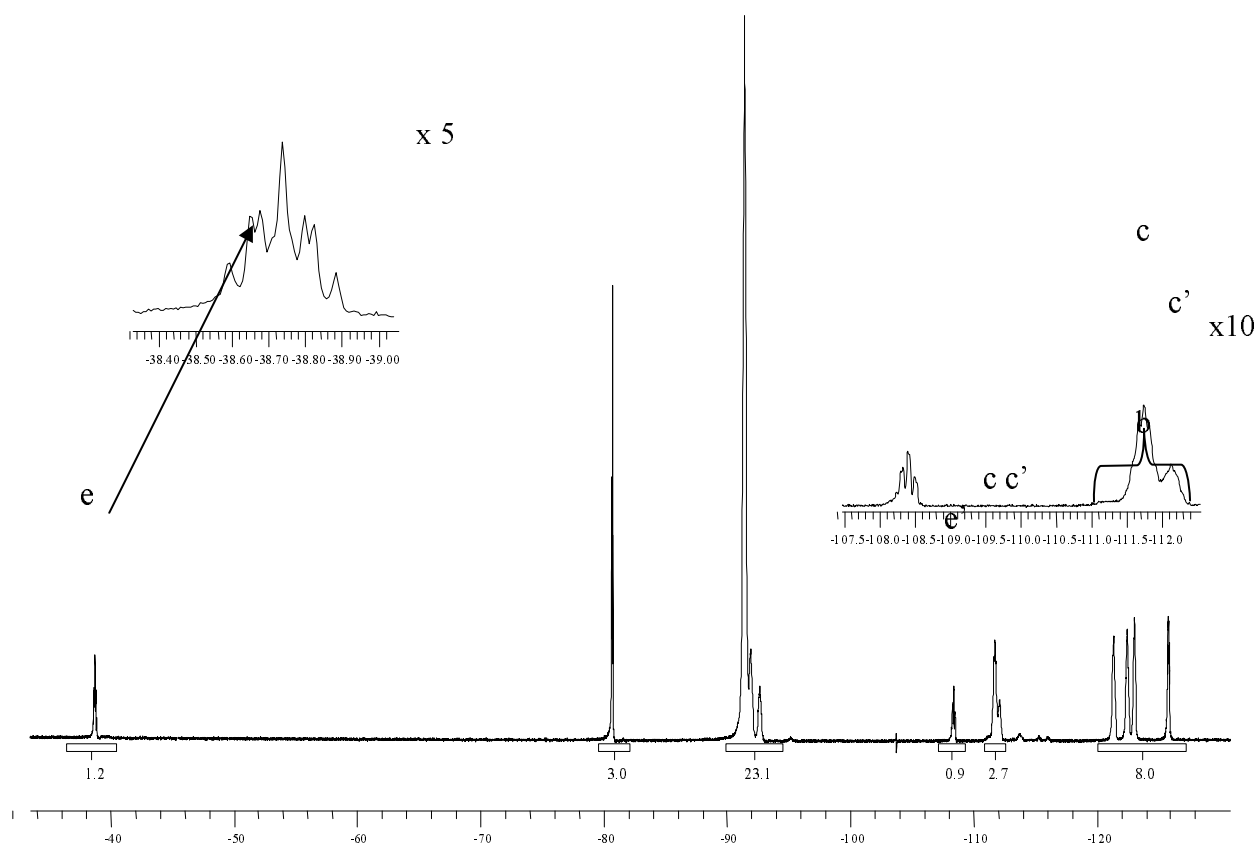
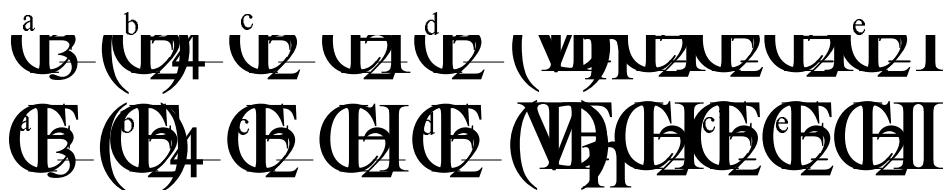


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Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{C}_6\text{F}_{13}\text{I}$: $[\text{VDF}]_0 : [\text{C}_6\text{F}_{13}\text{I}]_0 : [\text{Tert-butylperoxypivalate}]_0 = 100.0 : 6.6 : 0.6$ at 75°C .

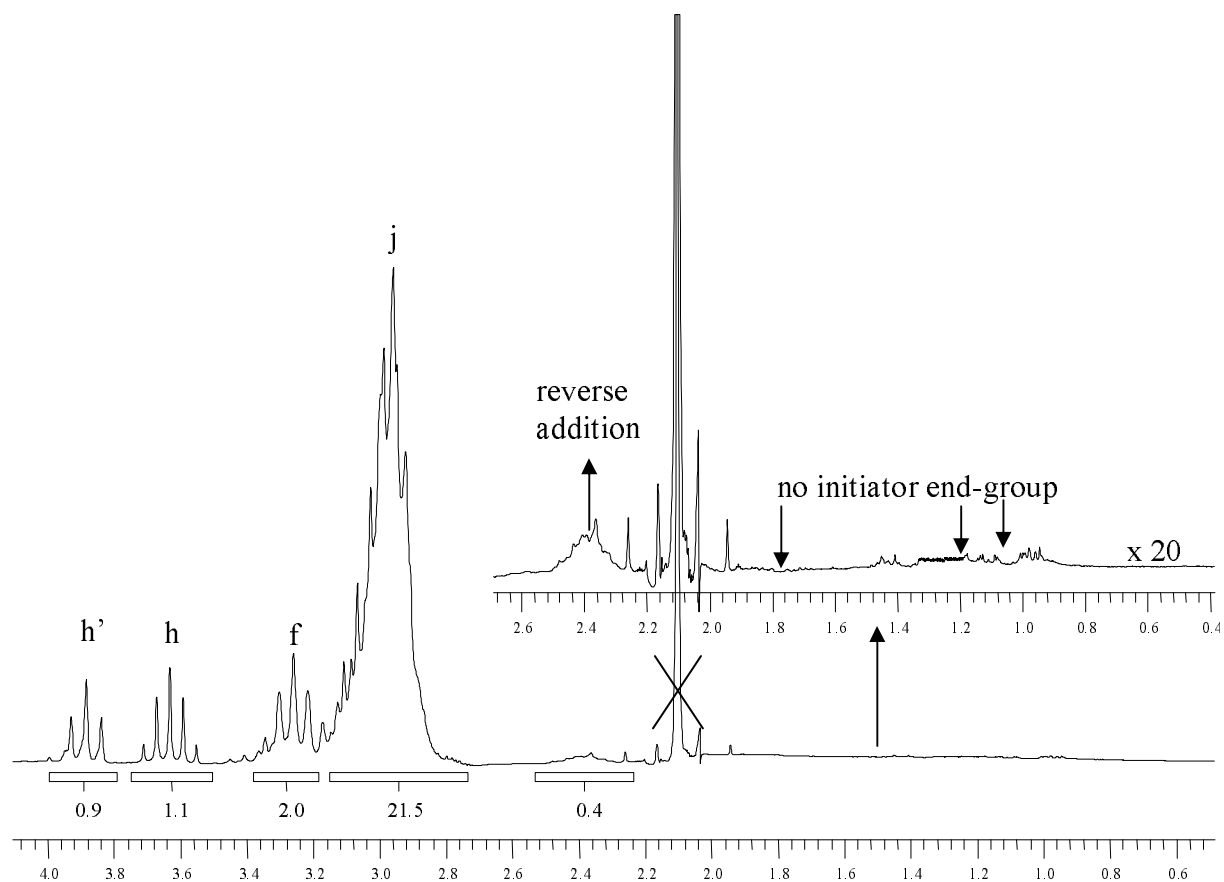
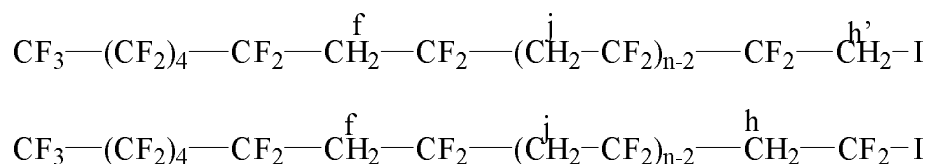


Figure 2. ¹H NMR spectrum of the poly(vinylidene fluoride)-I after precipitation (recorded in deuterated acetone; 200 MHz, 298 K) (Average number degree of polymerization ($\overline{\text{DP}}_n$) = 13).

Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{C}_6\text{F}_{13}\text{I} : [\text{VDF}]_0 : [\text{C}_6\text{F}_{13}\text{I}]_0 : [\text{Tert-butylperoxypivalate}]_0 = 100.0 : 6.6 : 0.6$ at 75 °C.

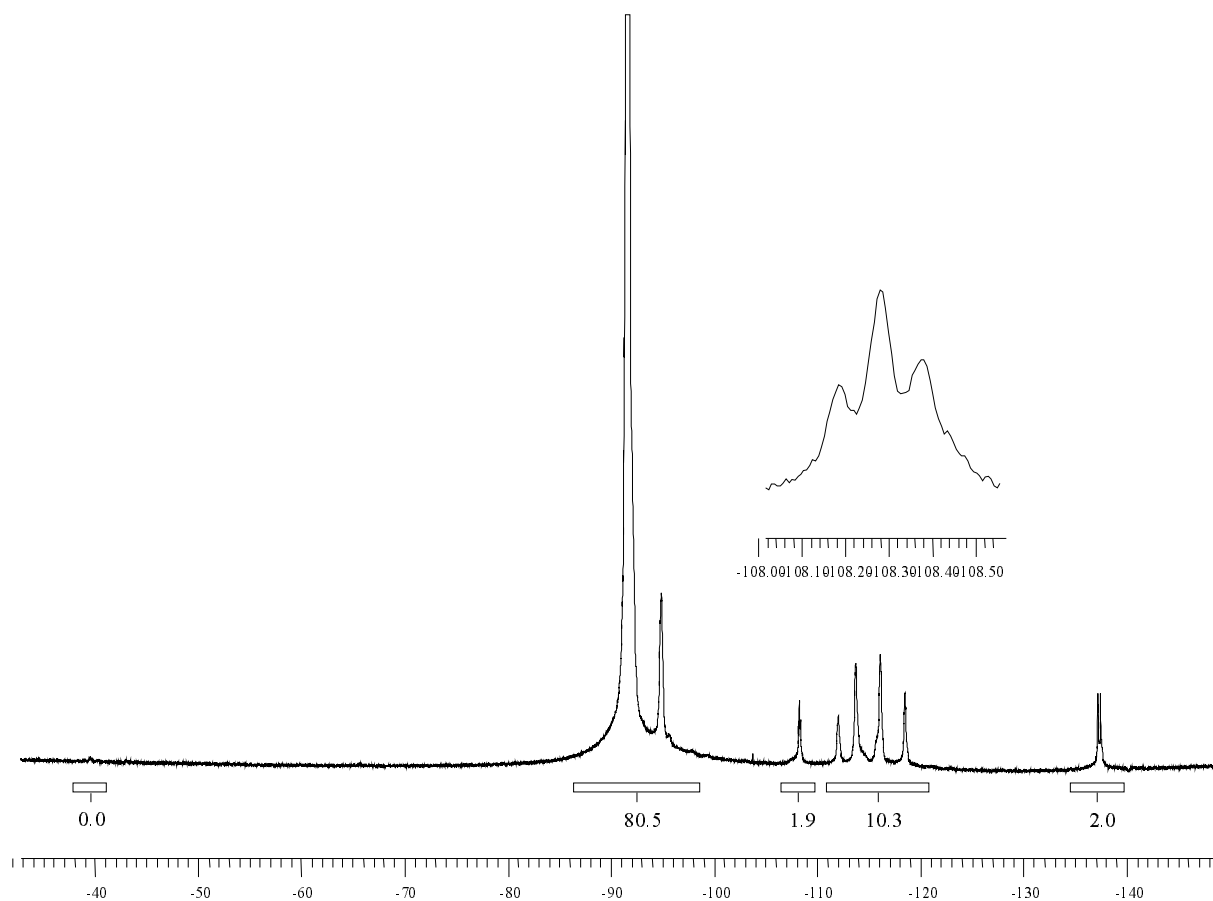


Figure 3. ^{19}F NMR spectrum of poly(vinylidene fluoride)-I obtained by *Iodine Transfer Polymerization* of vinylidene fluoride with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ (after precipitation and purification) (Average number degree of polymerization ($\overline{\text{DP}}_n$) = 35, calculated from Equation 8) (recorded in deuterated dimethylformamide; 250 MHz, 298 K).

Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$: $[\text{VDF}]:[\text{HC}_2\text{F}_4\text{-CH}_2\text{I}]:[\text{Tert-butylperoxypivalate}] = 100.0 : 6.6 : 0.6$ at 75°C .

Table Captions

Table 1. Iodine transfer polymerisation of fluoroalkenes for the synthesis of fluorinated Hard-b-Soft-b-Hard triblock copolymers (n.g. stands for not given).

a) VDF, HFP, TFE, CTFE, PMVE, FVA, E and P represent vinylidene fluoride, hexafluoropropene, tetrafluoroethylene, chlorotrifluoroethylene, perfluoromethyl-vinylether, perfluoro vinylacetic acid, ethylene, and propylene, respectively.

b) also tetrapolymerisation with less than 1 mol.% of $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{F}_{12}-\text{CH}=\text{CH}_2$.

c) also tetrapolymerisation with less than 1 mol.% of $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{F}_{12}-\text{CH}=\text{CH}_2$ / $\text{H}_2\text{C}=\text{CHC}_6\text{F}_{12}\text{C}_2\text{H}_4\text{I}$ / $\text{IC}_2\text{H}_4\text{C}_6\text{F}_{12}\text{C}_2\text{H}_4\text{I}$ mixture.

Table 2. Assignments of ^{19}F NMR chemical shifts in poly(vinylidene fluoride)-I. (s: singlet, d: doublet, t: triplet, m: multiplet).

Table 3. Assignments of ^1H NMR chemical shifts in poly(vinylidene fluoride)-I. (s: singlet; t: triplet; q: quintet; m: multiplet).

Table 4. Summary of average number degree of polymerization ($\overline{\text{DP}}_n$) for various concentrations in chain transfer agent (CTA: $\text{C}_6\text{F}_{13}\text{-I}$)

a- temperature : 75 °C; b- calculated by Equation 1; c- determined by ^{19}F and ^1H NMR (Equations 2 and 3); d- conversion of monomer assessed by gravimetry :

$$\alpha_{\text{VDF}} = \frac{\text{weight}_{\text{polymer}}}{\text{weight}_{\text{monomer}} + \text{weight}_{\text{C}_6\text{F}_{13}\text{I}}} \cdot 100; \text{ e- } -\text{CH}_2\text{CF}_2\text{-I or } -\text{CF}_2\text{CH}_2\text{-I functionalities assessed from}$$

^{19}F and ^1H NMR ; f- $-\text{CH}_2\text{CF}_2\text{-I}$ functionality determined from Equation 6.

Table 5. Variation of the functionality in $-\text{CF}_2\text{-I}$ for various fractions of oligomers (fractionation of poly(vinylidene fluoride)-I; (average number degree of polymerization, $\overline{\text{DP}}_n = 25$). a- assessed by ^1H NMR; b- $-\text{CH}_2\text{CF}_2\text{-I}$ functionality determined from ^{19}F NMR (Equation 4).

Table 6. Summary of average number degree of polymerization ($\overline{\text{DP}}_n$) for Iodine Transfer Polymerization reaction performed with various concentrations of $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$, and with two initiators [A_2] : [*Tert*-butylperoxypivalate] at 75°C and [2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane] at 135 °C.

a- calculated from Equation 2; b- determined by ^{19}F NMR (eq. 7); determined by ^1H NMR (eq. 8); d- monomer conversion measured by gravimetry (R massic yield) :

$$R = \frac{\text{weight}_{\text{polymer}}}{\text{weight}_{\text{monomer}} + \text{weight}_{\text{HC}_2\text{F}_4\text{CH}_2\text{I}}} \cdot 100; \text{ e- conversion of } \text{HC}_2\text{F}_4\text{CH}_2\text{I}; \text{ f- functionality in } \text{CF}_2\text{I}$$

(determined by ^{19}F NMR (from eq.4); g- chain percentage resulting from direct initiation (Eq. 9).

Soft block ^{a)}	% comonomers in soft block	Hard block	Soft / Hard Ratio (wt%)	T _g (°C)	T _m (°C)	Ref.
I[(VDF) _x HFP] _y I	n.g.	PVDF	n.g.	n.g.	160	14
I[(VDF) _x HFP] _y I	n.g.	poly(E-alt-TFE)	n.g.	n.g.	220	14
I[(CTFE) _x (VDF) _y] _z I	45/55	poly(E-co-CTFE)	85/15	-6	247	7
I[(CTFE) _x (VDF) _y] _z I	45/55	poly(E-co-TFE)	90/10	-8	252	7
I[(VDF) _x (FVA) _y] _z I	n.g.	PVDF	n.g.	n.g.	n.g.	14
I[(TFE) _x P] _y I	55/45	poly(E-co-TFE)	80/20	-1	267	9
I[(VDF) _x HFP(TFE) _y] _z I ^{b)c)}	56/19/25	PVDF	80/20	-12 to -15	165	11,12
I[(VDF) _x HFP(TFE) _y] _z I	35/40/25 (wt)	poly(E-alt-TFE)	n.g.	-8	222	14
I[(VDF) _x HFP(TFE) _y] _z I	50/30/20	poly(E-co-HFP-co-TFE)	85/15	n.g.	n.g.	7
I[(VDF) _x HFP(TFE) _y] _z I ^{b)}	54/21/25	poly(E-alt-TFE)	80/20	-13	266	11
I[(VDF) _x PMVE(TFE) _y] _z I ^{b)}	62/19/19	PVDF	80/20	-30	160	11,13
I[(VDF) _x PMVE(TFE) _y] _z I	73/17/10	poly(E-co-TFE)	72/28	-33	254	9
I[(VDF) _x PMVE(TFE) _y] _z I ^{b)}	n.g.	poly(E-co-TFE)	n.g.	-13 to -15	266	11,12
I[(VDF) _x PMVE(TFE) _y] _z I ^{b)}	57/23/20	poly(E-co-TFE-co-PMVE)	75/25	n.g.	180	13
I[(TFE) _x P(VDF) _y] _z I	n.g.	poly(E-co-TFE)	85/15	-13	262	9
I[(TFE) _x E(PMVE) _y] _z I	45/19/36	poly(E-co-TFE)	71/29	-16	245	9

Table 1. Iodine transfer polymerisation of fluoroalkenes for the synthesis of fluorinated Hard-b-Soft-b-Hard triblock copolymers (n.g. stands for not given).

a) VDF, HFP, TFE, CTFE, PMVE, FVA, E and P represent vinylidene fluoride, hexafluoropropene, tetrafluoroethylene, chlorotrifluoroethylene, perfluoromethylvinylether, perfluoro vinylacetic acid, ethylene, and propylene, respectively.

b) also tetrapolymerisation with less than 1 mol.% of H₂C=CH-C₆F₁₂-CH=CH₂.

c) also tetrapolymerisation with less than 1 mol.% of H₂C=CH-C₆F₁₂-CH=CH₂ / H₂C=CHC₆F₁₂C₂H₄I / IC₂H₄C₆F₁₂C₂H₄I mixture.

δ (ppm)	Signal	Assignment
-38.0	t ($^3J_{FH} = 7.0$ Hz) t ($^4J_{FF} = 9.8$ Hz)	-CH ₂ -CF ₂ I
-60.0	m	-CF ₂ -CF ₂ I
-82.0	m	CF ₃ -CF ₂ -
-91.0	m	-CH ₂ -CF ₂ -CH ₂ -CF ₂ -
-95.7	m	CH ₃ -CH ₂ -CF ₂ -
-108.0	m	CH ₃ -CF ₂ - -CF ₂ -CF ₂ -CH ₂ -I -CF ₂ -CF ₂ -CH ₂ -CF ₂ -
-112.0	m	(CH ₃) ₃ C-CF ₂ -CH ₂ -
-113.4	m	-CH ₂ -CF ₂ -CF ₂ -CH ₂ -CH ₂ -
-115.7	m	-CH ₂ -CF ₂ -CF ₂ -CH ₂ -CH ₂ -
-138.0	dm	HCF ₂ -CF ₂ -

Table 2. Assignments of ^{19}F NMR chemical shifts in poly(vinylidene fluoride)-I. (s: singlet, d: doublet, t: triplet, m: multiplet).

δ (ppm)	Signal	Assignment
1.0	s	(<u>CH₃</u>) ₃ CCH ₂ -CF ₂ -
1.2	t	<u>CH₃</u> -CH ₂ -CF ₂ -
1.3	s	(<u>CH₃</u>) ₃ CCF ₂ -CH ₂ -
1.8	t	<u>CH₃</u> -CF ₂ -CH ₂ -
2.3	m	-CH ₂ -CF ₂ -CF ₂ - <u>CH₂</u> - <u>CH₂</u> -CF ₂ -
2.9	m	-CH ₂ -CF ₂ - <u>CH₂</u> -CF ₂ - <u>CH₂</u> -CF ₂ - CH ₃ - <u>CH₂</u> -CF ₂ - (CH ₃) ₃ C <u>CH₂</u> -CF ₂ -
3.3	q	C ₆ F ₁₃ - <u>CH₂</u> -CF ₂ -
3.7	q	- <u>CH₂</u> -CF ₂ -I
3.9	q	-CF ₂ - <u>CH₂</u> -I
6.5	t(² J _{HF} = 49.6 Hz) t(³ J _{HF} = 4.0 Hz)	<u>H</u> CF ₂ CF ₂

Table 3. Assignments of ¹H NMR chemical shifts in poly(vinylidene fluoride)-I. (s: singlet; t: triplet; q: quintet; m: multiplet).

Run	Concentration ratios ^a [VDF] ₀ : [Chain transfer agent] ₀ : [Tert- butylperoxypivalate] ₀	Targeted ^b \overline{DP}_n ($\alpha=100$)	Experimental ^c \overline{DP}_n	α_{VDF} ^d (%)	functionality _{exp.} ^e				functionality _{theo.}
					-CF ₂ -I		-CH ₂ -I		-CF ₂ -I (%) ^f
					(%)	(%)	(%)	(%)	
¹⁹ F	¹ H	¹⁹ F	¹ H						
M1	100.0: 11.0: 1.1	9	6	70	75	78	25	22	77
M2	100.0: 10.0: 1.0	10	9	90	68	65	32	35	66
M3	100.0: 6.6: 0.6	15	13	70	60	55	46	35	54
M4	100.0: 3.3: 0.3	30	25	75	28	29	72	71	29

Table 4. Summary of average number degree of polymerization (\overline{DP}_n) for various concentrations in chain transfer agent (CTA: C₆F₁₃-I)

a- temperature : 75 °C; b- calculated by Equation 1; c- determined by ¹⁹F and ¹H NMR (Equations 2 and 3); d- conversion of monomer assessed by gravimetry :

$$\alpha_{VDF} = \frac{weight_{polymer}}{weight_{monomer} + weight_{C_6F_{13}}}.100; \text{ e- } -CH_2CF_2-I \text{ or } -CF_2CH_2-I \text{ functionalities assessed from}$$

¹⁹F and ¹H NMR ; f- -CH₂CF₂-I functionality determined from Equation 6.

Fractions	Initial \overline{DP}_n	Experimental ^a \overline{DP}_n of each fraction	Weight of the fraction (g)	functionality _{exp} (f _{exp})	
				-CF ₂ -I (%) ^b	
				¹ H	¹⁹ F
F1	25	5	10	0	0
F2	25	15	50	5	5
F3	25	35	40	50	45

Table 5. Variation of the functionality in -CF₂-I for various fractions of oligomers (fractionation of poly(vinylidene fluoride)-I; (average degree of polymerization, $\overline{DP}_n = 25$). a- assessed by ¹H NMR; b- -CH₂CF₂-I functionality determined by ¹⁹F NMR (Equation 4).

Reactions	Concentration ratios [VDF] ₀ : [HC ₂ F ₄ CH ₂ I] ₀ : [A ₂] ₀	T (°C)	Targeted ^a \overline{DP}_n	Experimental \overline{DP}_n	α_{VDF}^d (%)	α_{CTA}^e (%)	$f_{exp.}$ (CF ₂ -I) (%) ^f	(ϵ) ^g (%)
M5	100.0: 6.6: 0.6	75	15	46 ^b (35 ^c)	80	33	0	17
M6	100.0: 6.6: 0.6	135	15	32 ^b (28 ^c)	80	66	0	13
M7	100.0: 2.5: 0.2	75	35	70 ^b (60 ^c)	80	33	0	14
M8	100.0: 2.5: 0.2	135	35	42 ^b (38 ^c)	90	66	0	10

Table 6. Summary of average degree of polymerization (\overline{DP}_n) for Iodine Transfer Polymerization reaction performed with various concentrations of HC₂F₄CH₂I, and with two initiators [A₂] : [*Tert*-butylperoxypivalate] at 75°C and [2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane] at 135 °C.

a- calculated from Equation 2; b- determined by ¹⁹F NMR (eq. 7); determined by ¹H NMR (eq. 8); d- monomer conversion measured by gravimetry (R massic yield) :

$$R = \frac{weight_{polymer}}{weight_{monomer} + weight_{HC_2F_4CH_2I}} \cdot 100; \quad e- \text{ conversion of } HC_2F_4CH_2I; \quad f- \text{ functionality in } CF_2I$$

(determined by ¹⁹F NMR (from eq.4); g- chain percentage resulting from direct inintiation (Eq. 9).

SUPPORTING INFORMATION

Experimental part

Reactions in autoclave

ITP reaction with perfluorohexyl iodide of VDF at 75 °C.

A 160-mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer and a rupture disc, was degassed and pressurized with 30 bar of nitrogen to check eventual leaks. Then, a 20 mm Hg vacuum was operated for 30 min. Under vacuum, were transferred into the autoclave 0.43 g (2×10^{-3} mol) of *tert*-butylperoxypivalate, 8.92 g (2×10^{-2} mol) of perfluorohexyl iodide and 100 g of 1,1,1,3,3-pentafluorobutane. Then, by double weighing, 12.8 g (2×10^{-1} mol) of VDF were introduced in the mixture. Afterward, the autoclave was progressively heated to 75 °C. It was observed an exotherm of ca. 10 °C and an increase of pressure from 22 bar up to 28 bar and then a sharp drop of pressure until to 18 bar. After reaction, the autoclave was placed in an ice bath for about 60 minutes and 1.20 g of unreacted VDF were progressively released (the conversion of VDF was 90 % and the CTA conversion was 100 %) After opening the autoclave, about 120 g of a brown liquid were obtained. After evaporation of 1,1,1,3,3-pentafluorobutane, the sample was dissolved in DMF, which enables solubilization of low \overline{DP}_n (also soluble in acetone) and high \overline{DP}_n , and precipitated by adding water into the DMF solution. White powder was obtained in all cases and ^{19}F NMR led to a $\overline{DP}_n = 9$. (This \overline{DP}_n is a low value). The sample was characterized by ^{19}F and ^1H NMR spectroscopy.

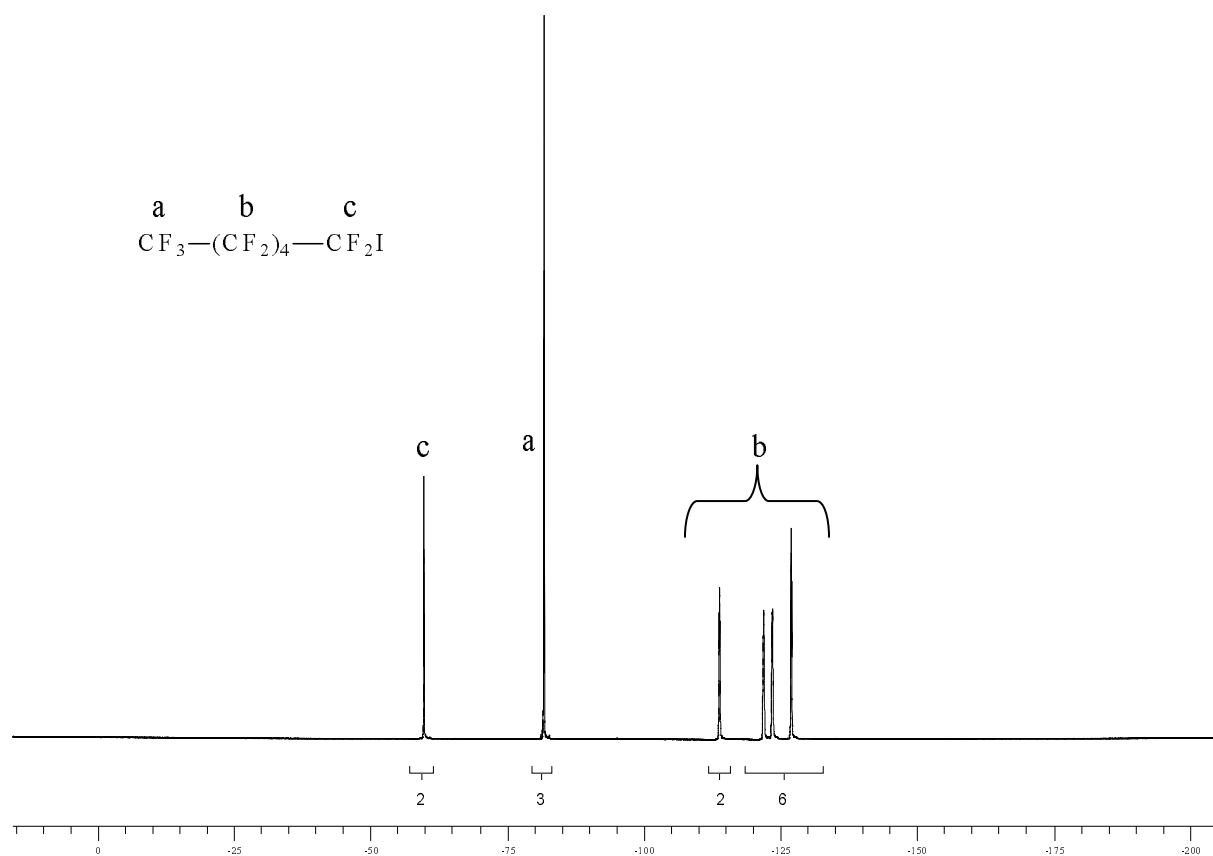


Figure 1. ^{19}F NMR spectrum of $\text{CF}_3\text{---}(\text{CF}_2)_4\text{---CF}_2\text{I}$ chain transfer constant (recorded in deuterated dimethylsulfoxide, 200 MHz, 298 K.).

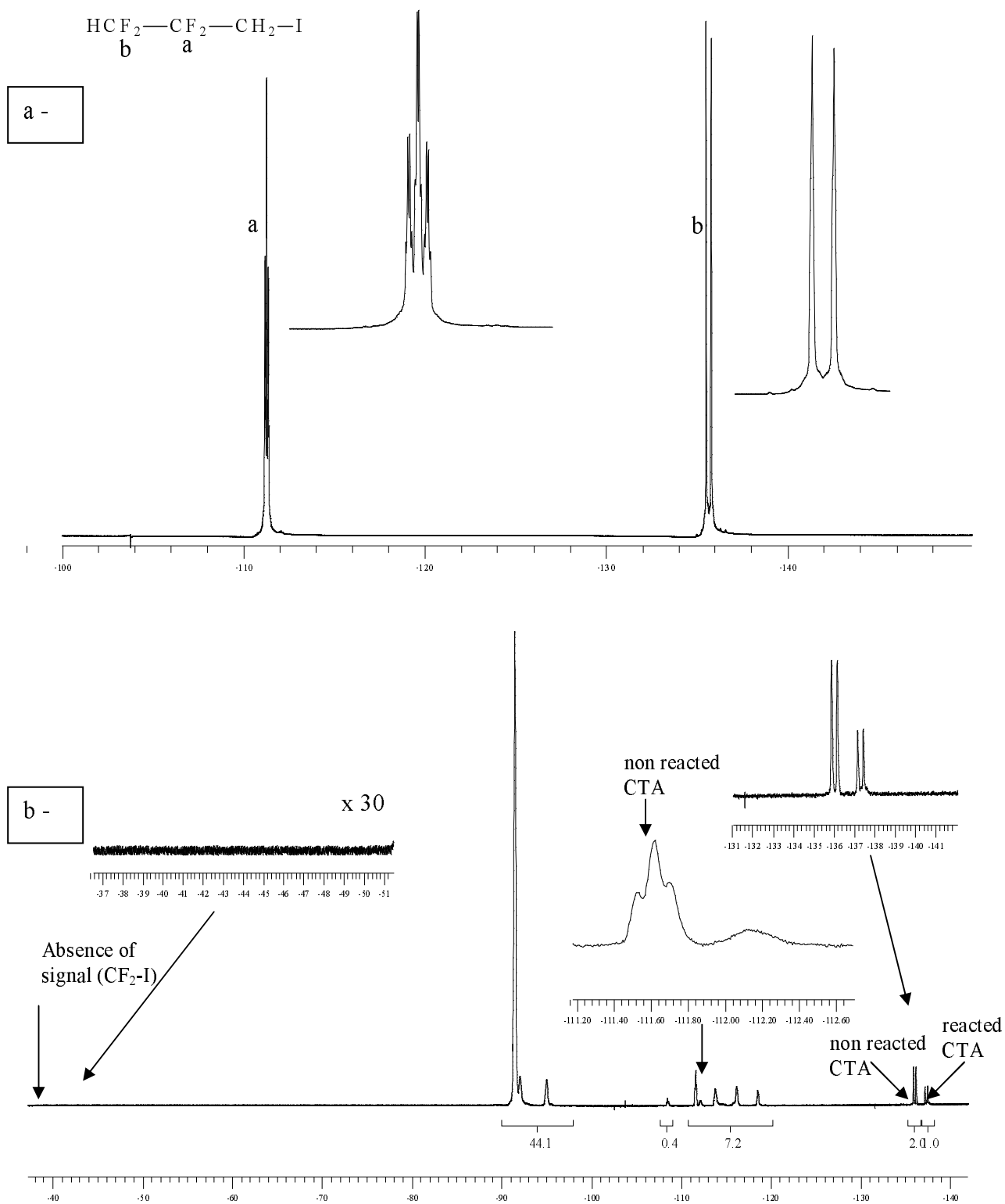


Figure 2. ^{19}F NMR spectra of (a) $(\text{HC}_2\text{F}_4\text{CH}_2\text{I})$ chain transfer agent, (b) sample produced by iodine transfer polymerization (ITP) of vinylidene fluoride (VDF) with $\text{HC}_2\text{F}_4\text{CH}_2\text{I}$ (recorded in deuterated dimethylformamide (DMF); 200 MHz, 298 K, $\overline{\text{DP}}_n = 32$).

Experimental conditions : ITP of VDF : $[\text{VDF}]_0$: $[\text{HC}_2\text{F}_4\text{CH}_2\text{I}]_0$: $[2,5\text{-bis}(\text{tert-butylperoxide})\text{-}2,5\text{-dimethylhexane}]_0 = 100.00 : 6.60 : 0.66$ at 75°C .

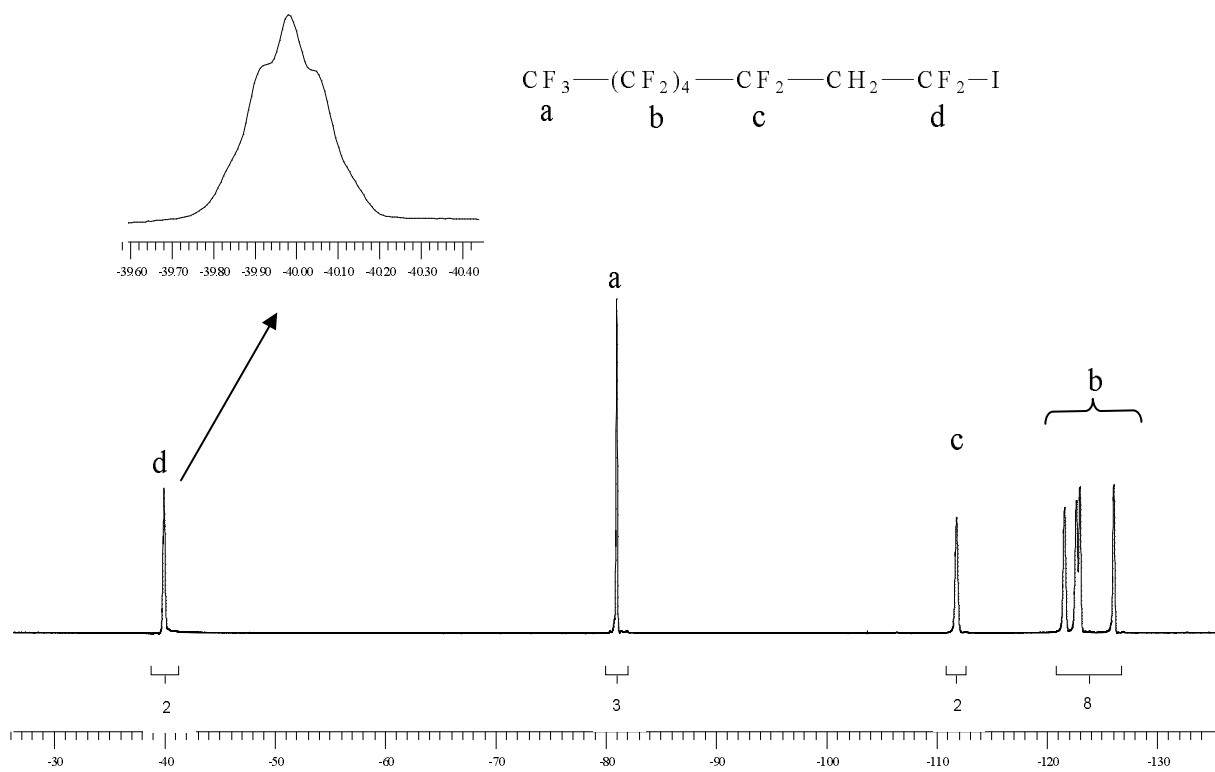


Figure 3. ^{19}F NMR spectrum of $\text{C}_6\text{F}_{13}\text{-(VDF)}_1\text{-I}$ monoadduct (200 MHz, 298 K, CDCl_3).